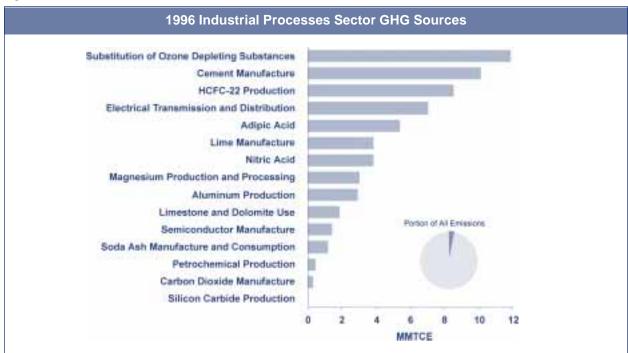# 3. Industrial Processes

Greenhouse gas emissions are produced as a by-product of various non-energy related industrial activities. That is, these emissions are produced directly from an industrial process itself and are not directly a result of energy consumed during the process. For example, raw materials can be chemically transformed from one state to another. This transformation often results in the release of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). The processes addressed in this chapter include cement production, lime manufacture, limestone and dolomite use (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash production and use, CO_2 manufacture, iron and steel production, ammonia manufacture, ferroalloy production, aluminum production, petrochemical production (including carbon black, ethylene, dicholoroethylene, styrene, and methanol), silicon carbide production, adipic acid production, and nitric acid production (see Figure 3-1).[1]

In addition to the three greenhouse gases listed above, there are also industrial sources of several classes of man-made fluorinated compounds called hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6). The present contribution of these gases to the radiative forcing effect of all anthropogenic greenhouse gases is

Figure 3-1

1996 Industrial Processes Sector GHG Sources

---

[1] Carbon dioxide emissions from iron and steel production, ammonia manufacture, ferroalloy production, and aluminum production are included under the Energy sector as part of fossil fuel combustion of industrial coking coal, natural gas, and petroleum coke.

small; however, because of their extremely long lifetimes, they will continue to accumulate in the atmosphere as long as emissions continue. Sulfur hexafluoride, itself, is the most potent greenhouse gas the IPCC has ever evaluated. Usage of these gases, especially HFCs, is growing rapidly as they are the primary substitutes for ozone depleting substances (ODS), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to ODS substitutes, HFCs, PFCs, and other fluorinated compounds are employed and emitted by a number of other industrial sources in the United States. These industries include aluminum production, HCFC-22 production, semiconductor manufacture, electric power transmission and distribution, and magnesium metal production and processing.

Total CO_2 emissions from industrial processes were approximately 17.3 MMTCE (63.3 Tg) in 1996. This amount accounted for only 1 percent of total U.S. CO_2 emissions. Methane emissions from petrochemical and silicon carbide production resulted in emissions of approximately 0.4 MMTCE (0.1 Tg) in 1996, which was less than 1 percent of U.S. CH_4 emissions. Nitrous oxide emissions from adipic acid and nitric acid production were 9.2 MMTCE (0.1 Tg) in 1996, or 9 percent of total U.S. N_2O emissions. In the same year, combined emissions of HFCs, PFCs and SF_6 totaled 34.7 MMTCE. Overall, emissions from the Industrial Processes sector increased by 35 percent from 1990 to 1996, and 8 percent in the last year alone.

Emission estimates are presented under this sector for several industrial processes that are actually accounted for within the Energy sector. Although CO_2 emissions from iron and steel production, ammonia manufacture, ferroalloy production, and aluminum production are not the result of the combustion of fossil fuels for energy, their associated emissions are captured in the fuel data for industrial coking coal, natural gas, industrial coking coal, and petroleum coke, respectively. Consequently, if all emissions were attributed to their appropriate sector, then emissions from energy would decrease by roughly 30 MMTCE in 1996, and industrial process emissions would increase by the same amount.

Greenhouse gases are also emitted from a number of industrial processes not addressed in this section. For example, caprolactam—a chemical feedstock for the manufacture of nylon 6,6—and urea production are believed to be industrial sources of N_2O emissions. However, emissions for these and other sources have not been estimated at this time due to a lack of information on the emission processes, manufacturing data, or both. As more information becomes available, emission estimates for these processes will be calculated and included in future greenhouse gas emission inventories, although their contribution is expected to be small.[2]

The general method employed to estimate emissions for industrial processes, as recommended by the Intergovernmental Panel on Climate Change (IPCC), generally involved multiplying production data for each process by an emission factor per unit of production. The emission factors used were either derived using calculations that assume precise and efficient chemical reactions or were based upon empirical data in published references. As a result, uncertainties in the emission coefficients can be attributed to, among other things, inefficiencies in the chemical reactions associated with each production process or to the use of empirically derived emission factors that are biased and, therefore, may not represent U.S. national averages. Additional sources of uncertainty specific to an individual source category are discussed in each section.

Table 3-1 summarizes emissions from the Industrial Processes sector in units of million metric tons of carbon equivalents (MMTCE), while unweighted gas emissions in teragrams (Tg) are provided in Table 3-2.

Cement Manufacture

Cement production is an energy and raw material intensive process resulting in the generation of substantial amounts of carbon dioxide (CO_2) from both the energy consumed in making the cement and the chemical process itself. Cement production accounts for about 2.4 percent of total global industrial and energy related CO_2 emissions (IPCC 1996). The United States is the world's third largest cement producer. Cement is pro-

Table 3-1: Emissions from Industrial Processes (MMTCE)

Gas/Source	1990	1991	1992	1993	1994	1995	1996
CO_2	14.9	14.5	14.6	15.1	15.9	16.8	17.3
Cement Manufacture	8.9	8.7	8.8	9.3	9.6	9.9	10.1
Lime Manufacture	3.3	3.2	3.3	3.4	3.5	3.7	3.8
Limestone and Dolomite Use	1.4	1.3	1.2	1.1	1.5	1.8	1.8
Soda Ash Manufacture and Consumption	1.1	1.1	1.1	1.1	1.1	1.2	1.2
Carbon Dioxide Manufacture	0.2	0.2	0.2	0.2	0.2	0.3	0.3
Iron and Steel Production*	23.9	19.2	20.7	21.0	21.6	22.2	21.6
Ammonia Manufacture*	6.3	6.4	6.7	6.4	6.6	6.5	6.6
Ferroalloy Production*	0.5	0.4	0.4	0.4	0.4	0.4	0.5
Aluminum Production*	1.6	1.7	1.6	1.5	1.3	1.4	1.4
CH_4	0.3	0.3	0.3	0.4	0.4	0.4	0.4
Petrochemical Production	0.3	0.3	0.3	0.4	0.4	0.4	0.4
Silicon Carbide Production	+	+	+	+	+	+	+
N_2O	8.1	8.3	8.0	8.4	8.9	9.0	9.2
Adipic Acid Production	4.7	4.9	4.6	4.9	5.2	5.2	5.4
Nitric Acid Production	3.4	3.3	3.4	3.5	3.7	3.7	3.8
HFCs, PFCs, and SF_6	22.2	21.6	23.0	23.4	25.9	30.8	34.7
Substitution of Ozone Depleting Substances	0.3	0.2	0.4	1.4	4.0	9.5	11.9
Aluminum Production	4.9	4.7	4.1	3.5	2.8	2.7	2.9
HCFC-22 Production	9.5	8.4	9.5	8.7	8.6	7.4	8.5
Semiconductor Manufacture	0.2	0.4	0.6	0.8	1.0	1.2	1.4
Electrical Transmission and Distribution	5.6	5.9	6.2	6.4	6.7	7.0	7.0
Magnesium Production and Processing	1.7	2.0	2.2	2.5	2.7	3.0	3.0
Total	**45.5**	**44.7**	**45.9**	**47.2**	**51.2**	**56.9**	**61.5**

+ Does not exceed 0.05 MMTCE
* Emissions from these sources are accounted for in the Energy sector and are not included in the Industrial Processes totals.
Note: Totals may not sum due to independent rounding.

duced in almost every state and is used in all of them. Carbon dioxide, emitted from the chemical process of cement production, represents one of the most significant sources of industrial CO_2 emissions in the United States.

During cement production, calcium carbonate ($CaCO_3$) is heated in a cement kiln at a temperature of 1,930°C (3,500°F) to form lime (i.e., calcium oxide or CaO) and CO_2. This process is known as calcination or calcining. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the by-product CO_2 being released to the atmosphere. The clinker is then allowed to cool, mixed with a small amount of gypsum, and used to make Portland and masonry cement. The production of masonry cement requires additional lime and, thus, results in additional CO_2 emissions. However, this additional lime is already accounted for in the Lime Manufacture section of this chapter; therefore, the additional emission from making masonry cement from clinker are not counted in this source's total. They are presented here for informational purposes only.

In 1996, U.S. clinker production—including Puerto Rico—totaled 73.1 teragrams (Tg), and U.S. masonry cement production reached 3.4 Tg (USGS 1997). The resulting emissions of CO_2 from clinker production were estimated to be 10.1 MMTCE (37.1 Tg), or less than 1 percent of total U.S. CO_2 emissions (Table 3-3). Emissions from masonry production from clinker raw material were estimated to be 0.02 MMTCE (0.08 Tg) in 1996, but are accounted for under Lime Manufacture.

After falling in 1991 by 2 percent from 1990 levels, cement production emissions have grown every year since. Overall, from 1990 to 1996 emissions increased by 14 percent. In 1996, output by cement plants increased 3 percent over 1995, to 73 Tg. In both the near and in-

2 See Annex Q for a discussion of emission sources excluded.

Table 3-2: Emissions from Industrial Processes (Tg)

Gas/Source	1990	1991	1992	1993	1994	1995	1996
CO_2	**54.6**	**53.3**	**53.7**	**55.3**	**58.4**	**61.5**	**63.3**
Cement Manufacture	32.6	31.9	32.1	33.9	35.4	36.1	37.1
Lime Manufacture	11.9	11.7	12.1	12.4	12.8	13.6	14.1
Limestone and Dolomite Use	5.1	4.9	4.5	4.1	5.3	6.5	6.7
Soda Ash Manufacture and Consumption	4.1	4.0	4.1	4.0	4.0	4.3	4.3
Carbon Dioxide Manufacture	0.8	0.8	0.9	0.9	0.9	1.0	1.1
Iron and Steel Production[a]	87.6	70.6	75.8	77.1	79.0	81.4	79.0
Ammonia Manufacture[a]	23.1	23.4	24.4	23.4	24.3	23.7	24.2
Ferroalloy Production[a]	1.8	1.6	1.6	1.5	1.6	1.6	1.7
Aluminum Production[a]	6.0	6.1	5.9	5.4	4.9	5.0	5.3
CH_4	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
Petrochemical Production	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Silicon Carbide Production	+	+	+	+	+	+	+
N_2O	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
Adipic Acid Production	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Nitric Acid Production	+	+	+	+	+	+	+
HFCs, PFCs, and SF_6	**M**	**M**	**M**	**M**	**M**	**M**	**M**
Substitution of Ozone Depleting Substances	M	M	M	M	M	M	M
Aluminum Production	M	M	M	M	M	M	M
HCFC-22 Production[b]	+	+	+	+	+	+	+
Semiconductor Manufacture	M	M	M	M	M	M	M
Electrical Transmission and Distribution[c]	+	+	+	+	+	+	+
Magnesium Production and Processing[c]	+	+	+	+	+	+	+

+ Does not exceed 0.05 Tg
M (Mixture of gases)
[a] Emissions from these sources are accounted for in the Energy sector and are not included in the Industrial Processes totals.
[b] HFC-23 emitted
[c] SF_6 emitted
Note: Totals may not sum due to independent rounding.

Table 3-3: CO_2 Emissions from Cement Production*

Year	MMTCE	Tg
1990	8.9	32.6
1991	8.7	31.9
1992	8.8	32.1
1993	9.3	33.9
1994	9.7	35.4
1995	9.9	36.1
1996	10.1	37.1

* Totals exclude CO_2 emissions from making masonry cement from clinker, which are accounted for under Lime Manufacture.

termediate terms, cement production in the United States is anticipated to grow only modestly (USGS 1996). Cement is a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic growth, will have considerable influence on cement production in the future.

Methodology

Carbon dioxide emissions from cement production are created by the chemical reaction of carbon-containing minerals (i.e., calcining limestone). While in the kiln, limestone is broken down into CO_2 and lime with the CO_2 released to the atmosphere. The quantity of the CO_2 emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of $CaCO_3$ (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO_2:

$$CaCO_3 + heat \rightarrow CaO + CO_2$$

Carbon dioxide emissions were estimated by applying an emission factor, in tons of CO_2 released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the average lime fraction for clinker of

64.6 percent (IPCC/UNEP/OECD/IEA 1997) and a constant reflecting the mass of CO_2 released per unit of lime. This yields an emission factor of 0.507 metric tons of CO_2 per metric ton of clinker produced. The emission factor was calculated as follows:

$$EF_{Clinker} = 0.646 \left[\frac{CaO \times 44.01 \text{ g/mole } CO_2}{56.08 \text{ g/mole } CaO} \right] = 0.507 \text{ tons/ } CO_2/\text{ton clinker}$$

Masonry cement requires additional lime over and above the lime used in clinker production. In particular, non-plasticizer additives such as lime, slag, and shale are added to the cement, increasing its weight by approximately 5 percent. Lime accounts for approximately 60 percent of this added weight. Thus, the additional lime is equivalent to roughly 2.86 percent of the starting amount of the product, since:

$$0.6 \times 0.05/(1 + 0.05) = 2.86\%$$

An emission factor for this added lime can then be calculated by multiplying this percentage (2.86 percent) by the molecular weight ratio of CO_2 to CaO (0.785) to yield 0.0224 metric tons of additional CO_2 emitted for every metric ton of masonry cement produced.

As previously mentioned, the CO_2 emissions from the additional lime added during masonry cement production were accounted for in the section on CO_2 emissions from Lime Manufacture. Thus, these emissions were estimated in this chapter for informational purposes only, and are not included in the cement emission totals.

Data Sources

The activity data for cement and clinker production (see Table 3-4) were taken from U.S. Geological Survey (USGS 1992, 1995, 1996, 1997); the 1996 figure was adjusted, as stated below, from USGS, *Mineral Industry Surveys: Cement in December 1996.* The data

Table 3-4: Cement Production (Thousand Metric Tons)

Year	Clinker	Masonry
1990	64,355	3,209
1991	62,918	2,856
1992	63,415	3,093
1993	66,957	2,975
1994	69,786	3,283
1995	71,257	3,603
1996	73,103	3,420

were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants. For 1996, clinker figures were not yet available. Thus, as recommended by the USGS, clinker production was estimated for 1996 by subtracting 5 percent from Portland cement production (Portland cement is a mixture of clinker and approximately 5 percent gypsum).

Uncertainty

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker and in the amount of lime added to masonry cement. For example, the lime content of clinker varies from 64 to 66 percent. Also, some amount of CO_2 is reabsorbed when the cement is used for construction. As cement reacts with water, alkaline substances such as calcium hydroxide are formed. During this curing process, these compounds may react with CO_2 in the atmosphere to create calcium carbonate. This reaction only occurs in roughly the outer 0.2 inches of surface area. Since the amount of CO_2 reabsorbed is thought to be minimal, it is not considered in this analysis. In addition, estimating emissions based on finished cement production for 1996 ignores the consideration that some domestic cement may be made from imported clinker.

Lime Manufacture

Lime, or calcium oxide (CaO), is an important manufactured product with many industrial, chemical, and environmental applications. Lime has historically ranked fifth in total production of all chemicals in the United States. Its major uses are in steel making, flue gas desulfurization (FGD), construction, pulp and paper manufacturing, and water purification. Lime production involves three main processes: stone preparation, calcination, and hydration. Carbon dioxide is generated during the calcination stage, when limestone—mostly calcium carbonate ($CaCO_3$)—is roasted at high temperatures in a kiln to produce CaO and CO_2. Some of the CO_2 generated during the production process, however, is recovered for use in sugar refining and precipitated calcium carbonate (PCC) production. The CO_2 is driven off as a gas and is normally emitted to the atmosphere.

Table 3-5: Net CO$_2$ Emissions from Lime Manufacture

Year	MMTCE
1990	3.3
1991	3.2
1992	3.3
1993	3.4
1994	3.5
1995	3.7
1996	3.8

Table 3-6: CO$_2$ Emissions from Lime Manufacture (Tg)

Year	Production	Recovered*	Net Emissions
1990	12.5	(0.5)	11.9
1991	12.3	(0.6)	11.7
1992	12.7	(0.6)	12.1
1993	13.2	(0.8)	12.4
1994	13.7	(0.9)	12.8
1995	14.5	(0.9)	13.6
1996	15.0	(0.9)	14.1

* For sugar refining and precipitated calcium carbonate production

Note: Totals may not sum due to independent rounding.

Lime production in the United States—including Puerto Rico—was reported to be 19.1 teragrams (Tg) in 1996 (USGS 1997). This resulted in CO$_2$ emissions of 3.8 MMTCE (14.1 Tg), or 0.2 percent of U.S. CO$_2$ emissions (see Table 3-5 and Table 3-6).

Domestic lime manufacture has increased every year since 1991, when it declined by 1 percent from 1990 levels. Production in 1996 increased 3 percent over that in 1995 to about 19 Tg. Commercial sales increased by 500,000 metric tons to a record high of 16.9 Tg (USGS 1997).

Overall, from 1990 to 1996, CO$_2$ emissions increased by 18 percent. This increasase is attributed in part to growth in demand for environmental applications. In 1993, the U.S. Environmental Protection Agency (EPA) completed regulations under the Clean Air Act capping sulfur dioxide (SO$_2$) emissions from electric utilities. This action resulted in greater lime consumption for flue gas desulfurization systems, which increased by 16 percent in 1993 (USGS 1994b). At the turn of the century, over 80 percent of lime consumed in the United States went for construction uses, but currently over 90 percent is consumed for chemical and industrial purposes, of which 28 percent are environmental uses (USGS 1997).

Methodology

During the calcination stage of lime manufacture, CO$_2$ is driven off as a gas and normally exits the system with the stack gas. The mass of CO$_2$ released per unit of lime produced can be calculated based on stoichiometry:

$$(44.01 \text{ g/mole CO}_2) \div (56.08 \text{ g/mole CaO}) = 0.785 \text{ g CO}_2/\text{g CaO}$$

Lime production in the United States was 19,100 thousand metric tons in 1996 (USGS 1997), resulting in potential CO$_2$ emissions of 15.0 Tg. Some of the CO$_2$ generated during the production process, however, was recovered for use in sugar refining and precipitated calcium carbonate (PCC) production. Combined lime manufacture by these producers was 1,428 thousand metric tons in 1996, generating 1.1 Tg of CO$_2$. Approximately 80 percent of this CO$_2$ was recovered.

Table 3-7: Lime Manufacture and Lime Use for Sugar Refining and PCC (Thousand Metric Tons)

Year	Production	Use
1990	15,859	826
1991	15,694	964
1992	16,227	1,023
1993	16,800	1,310
1994	17,400	1,377
1995	18,500	1,504
1996	19,100	1,428

Data Sources

The activity data for lime manufacture and lime consumption by sugar refining and precipitated calcium carbonate (PCC) for 1990 through 1992 (see Table 3-7) were taken from USGS (1991, 1992); for 1993 through 1994 from Michael Miller (1995); and for 1995 through 1996 from USGS (1997).

Uncertainty

The term "lime" is actually a general term that includes various chemical and physical forms of this commodity. Uncertainties in the emission estimate can be attributed to slight differences in the chemical composition of these products. For example, although much care is taken

to avoid contamination during the production process, lime typically contains trace amounts of impurities such as iron oxide, alumina and silica. Due to differences in the limestone used as a raw material, a rigid specification of lime material is impossible. As a result, few plants manufacture lime with exactly the same properties.

In addition, a portion of the CO_2 emitted during lime manufacture will actually be reabsorbed when the lime is consumed. In most processes that use lime (e.g., water softening), CO_2 reacts with the lime to create calcium carbonate. This is not necessarily true about lime consumption in the steel industry, however, which is the largest consumer of lime. A detailed accounting of lime use in the United States and further research into the associated processes are required to quantify the amount of CO_2 that is reabsorbed. As more information becomes available, this emission estimate will be adjusted accordingly.

In some cases, lime is generated from calcium carbonate by-products at paper mills and water treatment plants.[3] The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the paper industry, mills which employ the sulfate process (i.e., Kraft) consume lime in order to causticize a waste sodium carbonate solution (i.e., black liquor). Most sulfate mills recover the waste calcium carbonate after the causticizing operation and calcine it back into lime—thereby generating CO_2—for reuse in the pulping process. However, some of these mills capture the CO_2 released in this process to be used as precipitated calcium carbonate (PCC). Further research is necessary to determine to what extent CO_2 is released to the atmosphere through generation of lime by paper mills.

In the case of water treatment plants, lime is used in the softening process. Some large water treatment plants may recover their waste calcium carbonate and calcine it into quicklime for reuse in the softening process. Further research is necessary to determine the degree to which lime recycling is practiced by water treatment plants in the United States.

Limestone and Dolomite Use

Limestone ($CaCO_3$) and dolomite ($CaCO_3MgCO_3$)[4] are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy, glass manufacture, and environmental pollution control. Limestone is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Large deposits of limestone occur in nearly every state in the United States, and significant quantities are extracted for commercial use. For example, limestone can be used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization (FGD) systems for utility and industrial plants, or as a raw material in glass manufacturing. Limestone is heated during these processes, generating CO_2 as a by-product.

In 1996, approximately 11.8 Tg of limestone and 3.2 Tg of dolomite were used as flux stone in the chemical and metallurgical industries, in FGD systems, and for glass manufacturing (see Table 3-10). Overall, both limestone and dolomite usage resulted in aggregate CO_2 emissions of 1.8 MMTCE (6.7 Tg), or 0.1 percent of U.S. CO_2 emissions (see Table 3-8 and Table 3-9).

Emissions in 1996 increased 4 percent from the previous year. Though slightly decreasing in 1991, 1992, and 1993, CO_2 emissions from this source have since increased 33 percent from the 1990 baseline. In the near future, gradual increases in demand for crushed stone are anticipated based on the volume of work on highway and other infrastructure projects that are being financed by the Intermodal Surface Transportation Efficiency Act of 1991, the National Highway System Designation Act of 1995, and the overall growth in the U.S. economy (USGS 1996). The increases will be influenced, however, by construction activity for both publicly and privately funded projects.

---

[3] Some carbide producers may also regenerate lime from their calcium hydroxide by-products, nevertheless this process is not a source of CO_2. In making calcium carbide, quicklime is mixed with coke and heated in electric furnaces. The regeneration of lime in this process is done using a waste calcium hydroxide (hydrated lime) $[CaC_2 + 2H_2O \circledR C_2H_2 + Ca(OH)_2]$, not calcium carbonate $[CaCO_3]$. Thus, the calcium hydroxide is heated in the kiln to simply expel the water $[Ca(OH)_2 + heat \circledR CaO + H_2O]$ and no CO_2 is released to the atmosphere.

[4] Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

Table 3-8: CO$_2$ Emissions from Limestone & Dolomite Use (MMTCE)

Activity	1990	1991	1992	1993	1994	1995	1996
Flux Stone	0.8	0.7	0.6	0.5	0.8	1.1	1.1
Glass Making	0.1	+	0.1	0.1	0.1	0.1	0.2
FGD	0.5	0.6	0.5	0.5	0.6	0.6	0.6
Total	1.4	1.3	1.2	1.1	1.5	1.8	1.8

+ Does not exceed 0.05 MMTCE
Note: Totals may not sum due to independent rounding.

Table 3-9: CO$_2$ Emissions from Limestone & Dolomite Use (Tg)

Activity	1990	1991	1992	1993	1994	1995	1996
Flux Stone							
Limestone	2.6	2.3	2.0	1.6	2.1	2.5	2.7
Dolomite	0.4	0.4	0.3	0.3	0.8	1.4	1.5
Glass Making							
Limestone	0.2	0.2	0.2	0.3	0.4	0.4	0.4
Dolomite	NA	NA	NA	NA	NA	0.1	0.1
FGD	1.9	2.0	2.0	1.9	2.0	2.0	2.1
Total	5.1	4.9	4.5	4.1	5.3	6.5	6.7

NA (Not Available)
Note: Totals may not sum due to independent rounding.

Table 3-10: Limestone & Dolomite Consumption (Thousand Metric Tons)

Activity	1990	1991	1992	1993	1994	1995	1996
Flux Stone							
Limestone	5,797	5,213	4,447	3,631	4,792	5,734	6,052
Dolomite	932	838	737	632	1,739	2,852	3,010
Glass Making							
Limestone	430	386	495	622	809	958	1,011
Dolomite	NA	NA	NA	NA	NA	216	228
FGD	4,369	4,606	4,479	4,274	4,639	4,650	4,700

NA (Not Available)

Methodology

Carbon dioxide emissions were calculated by multiplying the amount of limestone consumed by an average carbon content for limestone, approximately 12.0 percent for limestone and 13.2 percent for dolomite (based on stoichiometry). Assuming that all of the carbon was released into the atmosphere, the appropriate emission factor was multiplied by the annual level of consumption for flux stone, glass manufacturing, and FGD systems to determine emissions.

Data Sources

Consumption data for 1990 through 1995 of limestone and dolomite used as flux stone and in glass manufacturing (see Table 3-10) were obtained from the USGS (1991, 1993, 1996). Data for 1996 were taken from USGS (1997). Consumption data for limestone used in FGD were taken from unpublished survey data in the Energy Information Administration's Form EI-767, "Steam Electric Plant Operation and Design Report," (EIA 1997).

The USGS reports production of total crushed stone annually, however, the breakdown of limestone and dolo-

mite production is only provided for odd years. Consumption figures for even years were estimated by assuming that limestone and dolomite account for the same percentage of total crushed stone for the given even year as the average of the percentages for the years before and after (exception: 1990 and 1996 consumption were estimated using the percentages for only 1991 and 1995, respectively).

It should be noted that there is a large quantity of crushed stone reported to the USGS under the category "unspecified uses". A portion of this consumption is believed to be limestone or dolomite used as flux stone and for glass manufacture. The quantity listed for "unspecified uses" was, therefore, allocated to each reported end-use according to each end-uses fraction of total consumption in that year.[5]

Uncertainty

Uncertainties in this estimate are due to variations in the chemical composition of limestone. In addition to calcite, limestone may contain smaller amounts of magnesia, silica, and sulfur. The exact specifications for limestone or dolomite used as flux stone vary with the pyrometallurgical process, the kind of ore processed, and the final use of the slag. Similarly, the quality of the limestone used for glass manufacturing will depend on the type of glass being manufactured. Uncertainties also exist in the activity data. Much of the limestone consumed in the United States is reported as "other unspecified uses;" therefore, it is difficult to accurately allocate this unspecified quantity to the correct end-uses. Furthermore, some of the limestone reported as "limestone" is believed to be dolomite, which has a higher carbon content than limestone.

Soda Ash Manufacture and Consumption

Soda ash (sodium carbonate, Na_2CO_3) is a white crystalline solid that is readily soluble in water and strongly alkaline. Commercial soda ash is used as a raw material in a variety of industrial processes and in many familiar consumer products such as glass, soap and detergents, paper, textiles, and food. It is used primarily as an alkali, either in glass manufacturing or simply as a material that reacts with and neutralizes acids or acidic substances. Internationally, two types of soda ash are produced—natural and synthetic. The United States produces only natural soda ash and is the largest soda ash-producing country in the world. Trona is the principal ore from which natural soda ash is made.

Only two states produce natural soda ash: Wyoming and California. Of these two states, only Wyoming has net emissions of CO_2. This difference is a result of the production processes employed in each state.[6] During the production process used in Wyoming, natural sources of sodium carbonate are heated and transformed into a crude soda ash that requires further refining. Carbon dioxide (CO_2) is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. In addition, CO_2 is also released when soda ash is consumed.

In 1996, CO_2 emissions from trona production were approximately 0.4 MMTCE (1.6 Tg). Soda ash consumption in the United States also generated about 0.7 MMTCE (2.7 Tg) of CO_2 in 1996. Total emissions from this source in 1996 were 1.2 MMTCE (4.3 Tg), or less than 0.1 percent of U.S. CO_2 emissions (see Table 3-11 and Table 3-12). Emissions have fluctuated since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 1996 decreased by 1 percent from the previous year, but have increased 3 percent since 1990.

The United States has the world's largest deposits of trona and represents about one-third of total world soda ash output. The distribution of soda ash by end-use in 1996 was glass making, 48 percent; chemical production, 27 percent; soap and detergent manufacturing, 12 percent; distributors, 5 percent; pulp and paper production, 3 percent;

---

5 This approach was recommended by USGS.

6 In California, soda ash is manufactured using sodium carbonate-bearing brines instead of trona ore. To extract the sodium carbonate, the complex brines are first treated with CO_2 in carbonation towers to convert the sodium carbonate into sodium bicarbonate, which will precipitate under these conditions. The precipitated sodium bicarbonate is then calcined back into sodium carbonate. Although CO_2 is generated as a by-product, the CO_2 is recovered and recycled for use in the carbonation stage and is never actually released.

Table 3-11: CO_2 Emissions from Soda Ash Manufacture and Consumption

Year	MMTCE
1990	1.1
1991	1.1
1992	1.1
1993	1.1
1994	1.1
1995	1.2
1996	1.2

Table 3-12: CO_2 Emissions from Soda Ash Manufacture and Consumption (Tg)

Year	Trona Production	Soda Ash Consumption	Total
1990	1.4	2.7	4.1
1991	1.4	2.6	4.0
1992	1.5	2.6	4.1
1993	1.4	2.6	4.1
1994	1.4	2.6	4.0
1995	1.6	2.7	4.3
1996	1.6	2.7	4.3

Note: Totals may not sum due to independent rounding.

flue gas desulfurization and miscellaneous, 2 percent each; and water treatment, 1 percent (USGS 1997).

Exports are a driving force behind increasing U.S. soda ash production capacity (USGS 1997). For example, the automotive manufacturing industry in South America is expanding considerably. This expansion will require additional quantities of flat glass for automotive windows in the estimated 2 million vehicles that are planned to be built by the end of the century (USGS 1997). Domestic soda ash consumption is also expected to rise in 1997.

Methodology

During the production process, trona ore is calcined in a rotary kiln and chemically transformed into a crude soda ash that requires further processing. Carbon dioxide and water are generated as a by-product of the calcination process. Carbon dioxide emissions from the calcination of trona can be estimated based on the following chemical reaction:

$$2(Na_3H(CO_3)_2 \; 2H_2O) \; \circledR \; 3Na_2CO_3 + 5H_2O + CO_2$$
$$\text{[trona]} \qquad\qquad \text{[soda ash]}$$

Based on this formula, approximately 10.27 metric tons of trona are required to generate one metric ton of CO_2. Thus, the 16.3 million metric tons of trona mined in 1996 for soda ash production (USGS 1997) resulted in CO_2 emissions of approximately 0.4 MMTCE (1.6 Tg).

Once manufactured, most soda ash is consumed in glass and chemical production, with minor amounts in soap and detergents, pulp and paper, flue gas desulfurization and water treatment. As soda ash is processed for these purposes, additional CO_2 is usually emitted. In these applica-

Table 3-13: Soda Ash Manufacture and Consumption (Thousand Metric Tons)

Year	Trona Production	Soda Ash Consumption
1990	14,734	6,527
1991	14,674	6,287
1992	14,900	6,360
1993	14,500	6,350
1994	14,600	6,240
1995	16,500	6,510
1996	16,300	6,410

tions, it is assumed that one mole of carbon is released for every mole of soda ash used. Thus, approximately 0.113 metric tons of carbon (or 0.415 metric tons of CO_2) are released for every metric ton of soda ash consumed.

Data Sources

The activity data for trona production and soda ash consumption (see Table 3-13) were taken from USGS (1993, 1994, 1995, 1997). Soda ash production and inventory data were collected by the USGS from voluntary surveys of the U.S. soda ash industry. All six of the soda ash operations in the United States completed surveys to provide production and consumption data to the USGS.

---

[7] It is unclear to what extent the CO_2 used for EOR will be re-released. For example, the CO_2 used for EOR is likely to show up at the wellhead after a few years of injection (Hangebrauk et al. 1992). This CO_2, however, is typically recovered and re-injected into the well. More research is required to determine the amount of CO_2 that in fact escapes. For the purposes of this analysis, it is assumed that all of the CO_2 remains sequestered.

Uncertainty

Emissions from soda ash consumption are dependent upon the type of processing employed by each end-use; however, specific information characterizing the emissions from each end-use is limited. Therefore, uncertainty exists as to the accuracy of the emission factors.

Carbon Dioxide Manufacture

Carbon dioxide (CO_2) is used for a variety of applications, including food processing, chemical production, carbonated beverages, and enhanced oil recovery (EOR). Carbon dioxide used for EOR is injected into the ground to increase reservoir pressure, and is therefore considered sequestered.[7] For the most part, however, CO_2 used in non-EOR applications will eventually enter the atmosphere.

Carbon dioxide is produced from a small number of natural wells, as a by-product from the production of chemicals (e.g., ammonia), or separated from crude oil and natural gas. Depending on the raw materials that are used, the by-product CO_2 generated during these production processes may already be accounted for in the CO_2 emission estimates from fossil fuel consumption (either during combustion or from non-fuel uses). For example, ammonia is manufactured using primarily natural gas as a feedstock. Carbon dioxide emissions from this process are accounted for in the Energy sector under Fossil Fuel Combustion and therefore are not included here.

In 1996, CO_2 emissions from this source were approximately 0.3 MMTCE (1.1 Tg), or less than 0.1 percent of U.S. CO_2 emissions (see Table 3-14). This amount represents an increase of 18 percent from the previous year and is 43 percent higher than CO_2 emissions in 1990, which totaled 0.2 MMTCE. Carbon dioxide demand in the merchant market is expected to expand 4.2 percent annually through 1998 (Freedonia Group 1994).

Methodology

Carbon dioxide emission estimates were based on CO_2 consumption with the assumption that the end-use applications, except enhanced oil recovery, eventually release 100 percent of the CO_2 into the atmosphere. Carbon dioxide

Table 3-14: CO_2 Emissions from Carbon Dioxide Manufacture

Year	MMTCE	Tg
1990	0.2	0.8
1991	0.2	0.8
1992	0.2	0.9
1993	0.2	0.9
1994	0.2	0.9
1995	0.3	1.0
1996	0.3	1.1

consumption for uses other than enhanced oil recovery was about 5.7 teragrams in 1996 (Ita 1997). The Freedonia Group estimates that, in the United States, there is a 80 to 20 percent split between CO_2 produced as a by-product and CO_2 produced from natural wells. Thus, emissions are equal to 20 percent of CO_2 consumption. The remaining 80 percent was assumed to already be accounted for in the CO_2 emission estimates from other categories (the most important being Fossil Fuel Combustion).

Data Sources

Carbon dioxide consumption data (see Table 3-15) were obtained from Freedonia Group Inc. (1994, 1996). Data for 1996 were obtained by personal communication with Paul Ita of the Freedonia Group Inc. (1997). Percent of carbon dioxide produced from natural wells was obtained from Freedonia Group Inc. (1991).

Table 3-15: Carbon Dioxide Consumption

Year	Thousand Metric Tons
1990	4,000
1991	4,200
1992	4,410
1993	4,559
1994	4,488
1995	4,842
1996	5,702

Uncertainty

Uncertainty exists in the assumed allocation of carbon dioxide manufactured from fossil fuel by-products (80 percent) and carbon dioxide produced from wells (20 percent). In addition, it is possible that CO_2 recovery exists in particular end-use sectors. Contact with

several organizations did not provide any information regarding recovery. More research is required to determine the quantity, if any, that may be recovered.

Iron and Steel Production

The production of iron and steel emits CO_2. Iron is produced by first reducing iron oxide (ore) with metallurgical coke in a blast furnace to produce pig iron (impure iron of about 4 to 4.5 percent carbon by weight). Carbon dioxide is produced as the coke used in the process is oxidized. Steel (less than 2 percent carbon by weight) is produced from pig iron in a variety of specialized steel furnaces. The majority of CO_2 emissions come from the production of iron, with smaller amounts evolving from the removal of carbon from pig iron to produce steel.

Additional CO_2 emissions also occur from the use of limestone or dolomite flux; however, these emissions are accounted for under Limestone and Dolomite Use.

Emissions of CO_2 from iron and steel production in 1996 were 21.6 MMTCE (79.0 Tg), falling from a high of 23.9 MMTCE (87.6 Tg) in 1990. Emissions fluctuated significantly in this period. CO_2 emissions from this source are not included in totals for the Industrial Processes sector because these emissions are accounted for with Fossil Fuel Combustion emissions from industrial coking coal in the Energy sector.[8] Emissions estimates are presented here for informational purposes only (see Table 3-16).

Table 3-16: CO_2 Emissions from Iron and Steel Production

Year	MMTCE	Tg
1990	23.9	87.6
1991	19.2	70.6
1992	20.6	75.8
1993	21.0	77.1
1994	21.6	79.0
1995	22.2	81.4
1996	21.6	79.0

Methodology

Carbon dioxide emissions were calculated by multiplying annual estimates of pig iron production by the ratio of CO_2 emitted per unit of iron produced (1.6 metric ton CO_2/ton iron). The emission factor employed was applied to both pig iron production and integrated pig iron plus steel production; therefore, emissions were estimated using total U.S. pig iron production for all uses including making steel.

Data Sources

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 1996 (see Table 3-17) came from the U.S. Geological Survey's (USGS) *Minerals Yearbook: Volume I-Metals and Minerals* (USGS 1994, 1996).

Table 3-17: Pig Iron Production

Year	Thousand Metric Tons
1990	54,750
1991	44,100
1992	47,400
1993	48,200
1994	49,400
1995	50,900
1996	49,400

Uncertainty

The emission factor employed was assumed to be applicable to both pig iron production and integrated pig iron plus steel production. This assumption was made because the uncertainty in the factor is greater than the additional emissions generated when steel is produced from pig iron. Using plant-specific emission factors would yield a more accurate estimate, but these factors were not available. The most accurate alternative would be to calculate emissions based on the amount of reducing agent used, rather than on the amount of iron or steel produced; however, these data were also not available.

---

[8] Although the CO_2 emissions from the use of industrial coking coal as a reducing agent should be included in the Industrial Processes sector, information to distinguish individual non-fuel uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

Ammonia Manufacture

Emissions of CO_2 occur during the production of ammonia. In the United States, roughly 98 percent of synthetic ammonia is produced by catalytic steam reforming of natural gas, and the remainder is produced using naphtha (a petroleum fraction) or the electrolysis of brine at chlorine plants (EPA 1997). The former two fossil fuel-based reactions produce carbon monoxide and hydrogen gas. (The latter reaction does not lead to CO_2 emissions.) Carbon monoxide (CO) is transformed into CO_2 in the presence of a catalyst (usually a metallic oxide) during the process. The hydrogen gas is diverted and combined with nitrogen gas to produce ammonia. The CO_2, included in a gas stream with other process impurities, is absorbed by a scrubber solution. In regenerating the scrubber solution, CO_2 is released.

$$(\text{catalyst})$$
$$CH_4 + H_2O \rightarrow 4H_2 + CO_2$$
$$3H_2 + N_2 \rightarrow 2NH_3$$

Emissions of CO_2 from ammonia production in 1996 were 6.6 MMTCE (24.2 Tg). For the 1990 through 1996 period, emissions fluctuated within a range of 6.3 to 6.7 MMTCE (23.1 to 24.4 Tg). Carbon dioxide emissions from this source are not included in totals for the Industrial Processes sector because these emissions are accounted for with Fossil Fuel Combustion of natural gas in the Energy sector.[9] Emissions estimates are presented here for informational purposes only (see Table 3-18).

Table 3-18: CO_2 Emissions from Ammonia Manufacture

Year	MMTCE	Tg
1990	6.3	23.1
1991	6.4	23.4
1992	6.7	24.4
1993	6.4	23.4
1994	6.6	24.3
1995	6.5	23.7
1996	6.6	24.2

Methodology

Emissions of CO_2 were calculated by multiplying annual estimates of ammonia production by an emission factor (1.5 ton CO_2/ton ammonia). It was assumed that all ammonia was produced using catalytic steam reformation, although small amounts may have been produced using chlorine brines. The actual amount produced using this latter method is not known, but assumed to be small.

Data Sources

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data (see Table 3-19) came from the Census Bureau of the U.S. Department of Commerce (Census Bureau 1997).

Table 3-19: Ammonia Manufacture

Year	Metric tons
1990	15,425,394
1991	15,573,812
1992	16,260,834
1993	15,599,485
1994	16,210,848
1995	15,787,276
1996	16,113,777

Uncertainty

It is uncertain how accurately the emission factor used represents an average across all ammonia plants. By using an alternative method of estimating emissions from ammonia production that requires data on the consumption of natural gas at each ammonia plant, more accurate estimates could be calculated. However, these consumption data are often considered confidential and are difficult to acquire. All ammonia production in this analysis was assumed to be from the same process; however, actual emissions could differ because processes other than catalytic steam reformation may have been used.

---

[9] Although the CO_2 emissions from the use of natural gas as a feedstock should be included in the Industrial Processes sector, information to distinguish individual non-fuel uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

Ferroalloy Production

Carbon dioxide is emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements often including silicon, manganese, and chromium. When incorporated in alloy steels, ferroalloys are used to alter the material properties of the steel. Estimates from two types of ferrosilicon (50 and 75 percent silicon) and silicon metal (about 98 percent silicon) have been calculated. Emissions from the production of ferrochromium and ferromanganese are not included here because of the small number of manufacturers of these materials. As a result, government information disclosure rules prevent the publication of production data for them. Similar to emissions from the production of iron and steel, CO_2 is emitted when coke is oxidized during a high-temperature reaction with iron and the selected alloying element. Due to the strong reducing environment, CO is initially produced. The CO is eventually oxidized, becoming CO_2. A representative reaction equation for the production of 50 percent ferrosilicon is given below:

$$Fe_2O_3 + 2SiO_2 + 7C \rightarrow 2FeSi + 7CO$$

Emissions of CO_2 from ferroalloy production in 1996 were 0.5 MMTCE (1.7 Tg). From 1990 through 1996, emissions fluctuated within a range of 0.4 to 0.5 MMTCE (1.5 to 1.8 Tg). Carbon dioxide emissions from this source are not included totals for the Industrial Processes sector because these emissions are accounted for in the calculations of industrial coking coal combustion under the Energy sector.[10] Emission estimates are presented here for informational purposes only (see Table 3-20).

Table 3-20: CO_2 Emissions from Ferroalloy Production

Year	MMTCE	Tg
1990	0.5	1.8
1991	0.4	1.6
1992	0.4	1.6
1993	0.4	1.5
1994	0.4	1.6
1995	0.4	1.6
1996	0.5	1.7

Methodology

Emissions of CO_2 were calculated by multiplying annual estimates of ferroalloy production by material-specific emission factors. Emission factors were applied to production data for ferrosilicon 50 and 75 percent (2.35 and 3.9 metric ton CO_2/metric ton, respectively) and silicon metal (4.3 metric ton CO_2/metric ton). It was assumed that all ferroalloy production was produced using coking coal, although some ferroalloys may have been produced with wood, biomass, or graphite carbon inputs.

Data Sources

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 1996 (see Table 3-21) came from the *Minerals Yearbook: Volume I—Metals and Minerals* published in USGS (1991, 1992, 1993, 1994, 1995, 1996, 1997).

Table 3-21: Production of Ferroalloys (Metric Tons)

Year	Ferrosilicon 50%	Ferrosilicon 75%	Silicon Metal
1990	321,385	109,566	145,744
1991	230,019	101,549	149,570
1992	238,562	79,976	164,326
1993	199,275	94,437	158,000
1994	198,000	112,000	164,000
1995	181,000	128,000	163,000
1996	182,000	132,000	175,000

Uncertainty

Although some ferroalloys may be produced using wood or biomass as a carbon source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood would not be counted under this source because wood-based carbon is of biogenic origin.[11] Emissions from ferroalloys produced with graphite inputs would be counted in national totals, but may generate differing amounts of CO_2 per unit of ferroalloy produced compared to the use of coking coal. As with emissions from iron and steel production, the most accurate method for these estimates would be basing calculations on the amount of reducing

---

[10] Although the CO_2 emissions from the use of industrial coking coal as a reducing agent should be included in the Industrial Processes sector, information to distinguish individual non-fuel uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

[11] Emissions and sinks of biogenic carbon are accounted for under the Land-Use Change and Forestry sector.

agent used in the process, rather than on the amount of ferroalloys produced. Again, these data were unavailable.

Petrochemical Production

Small amounts of methane (CH_4) are released during the production of petrochemicals. Emissions are calculated here from the production of five chemicals: carbon black, ethylene, ethylene dichloride, styrene, and methanol. Emissions of CH_4 from petrochemical production in 1996 were 0.4 MMTCE (73 Gg), or 0.2 percent of U.S. CH_4 emissions (see Table 3-22). Production levels of all five chemicals increased from 1990 to 1996.

Table 3-22: CH_4 Emissions from Petrochemical Production

Year	MMTCE	Gg
1990	0.3	55
1991	0.3	57
1992	0.3	60
1993	0.4	65
1994	0.4	70
1995	0.4	70
1996	0.4	73

Methodology

Emissions of CH_4 were calculated by multiplying annual estimates of chemical production by an emission factor. The following factors were used: 11 kg CH_4/metric ton carbon black, 1 kg CH_4/metric ton ethylene, 0.4 kg CH_4/metric ton ethylene dichloride, 4 kg CH_4/metric ton styrene, and 2 kg CH_4/metric ton methanol. These emission factors were based upon measured material balances. Although the production of other chemicals may also result in methane emissions, there were not sufficient data to estimate their emissions.

Data Sources

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Annual production data (see Table 3-23) came from the Chemical Manufacturers Association *Statistical Handbook* (CMA 1997).

Uncertainty

The emission factors used here were based on a limited number of studies. Using plant-specific factors instead of average factors would increase the accuracy of the emissions estimates, however, such data were not available. There may also be other significant sources of methane arising from chemical production activities which have not been included in these estimates.

Silicon Carbide Production

Methane is emitted from the production of silicon carbide, a material used as an industrial abrasive. To make silicon carbide (SiC), quartz (SiO_2) is reacted with carbon in the form of petroleum coke. Methane is produced during this reaction from volatile compounds in the petroleum coke. Although CO_2 is also emitted from this production process, the requisite data were unavailable for these calculations. Regardless, they are already accounted for under CO_2 from Fossil Fuel Combustion in the Energy sector. Emissions of CH_4 from silicon carbide production in 1996 (see Table 3-24) were less than 0.1 MMTCE (1 Gg).

Methodology

Emissions of CH_4 were calculated by multiplying annual estimates of silicon carbide production by an emission factor (11.6 kg CH_4/metric ton silicon carbide). This emission factor was derived empirically from measure-

Table 3-23: Production of Selected Petrochemicals (Metric Tons)

Chemical	1990	1991	1992	1993	1994	1995	1996
Carbon Black	1,306,368	1,224,720	1,365,336	1,451,520	1,492,344	1,524,096	1,560,384
Ethylene	16,541,885	18,124,042	18,563,126	18,382,594	20,200,622	19,470,326	20,343,960
Ethylene Dichloride	6,282,360	6,220,670	6,872,040	8,141,213	8,482,320	7,830,950	8,595,720
Styrene	3,636,965	3,680,510	4,082,400	4,565,030	5,112,072	5,166,504	5,386,954
Methanol	3,784,838	3,948,134	3,665,995	4,781,851	4,904,323	5,122,958	5,261,760

Table 3-24: CH$_4$ Emissions from Silicon Carbide Production

Year	MMTCE	Gg
1990	+	1
1991	+	1
1992	+	1
1993	+	1
1994	+	1
1995	+	1
1996	+	1

+ Does not exceed 0.05 MMTCE

ments taken at Norwegian silicon carbide plants (IPCC/UNEP/OECD/IEA 1997).

Data Sources

The emission factor was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Production data for 1990 through 1996 (see Table 3-25) came from the *Minerals Yearbook: Volume I-Metals and Minerals* published in USGS (1991, 1992, 1993, 1994, 1995, 1996, 1997).

Table 3-25: Production of Silicon Carbide

Year	Metric Tons
1990	105,000
1991	78,900
1992	84,300
1993	74,900
1994	84,700
1995	75,400
1996	73,600

Uncertainty

The emission factor used here was based on one study of Norwegian plants. The applicability of this factor to average U.S. practices at silicon carbide plants is uncertain. The most accurate alternative would be to calculate emissions based on the quantity of petroleum coke used during the production process rather than on the amount of silicon carbide produced. Again, these data were unavailable.

Adipic Acid Production

Adipic acid production has been identified as a significant anthropogenic source of nitrous oxide (N$_2$O) emissions. Adipic acid is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Commercially, it is the most important of the aliphatic dicarboxylic acids, which are used to manufacture polyesters. Ninety percent of all adipic acid produced in the United States is used in the production of nylon 6,6. It is also used to provide some foods with a "tangy" flavor.

Adipic acid is produced through a two-stage process during which N$_2$O is generated in the second stage. This second stage involves the oxidation of ketone-alcohol with nitric acid. Nitrous oxide is generated as a by-product of this reaction and is emitted in the waste gas stream. In the United States, this waste gas is treated to remove nitrogen oxides (NO$_x$), other regulated pollutants, and in some cases N$_2$O. There are currently four plants in the United States that produce adipic acid. Since 1990, two of these plants have employed emission control measures destroying roughly 98 percent of the N$_2$O in their waste gas stream before it is released to the atmosphere (Radian 1992). It is expected that all adipic acid production plants will have N$_2$O emission controls in place and operating by the end of 1997, as a result of a voluntary agreement among producers.

Adipic acid production for 1996 was estimated to be 835 thousand metric tons. Nitrous oxide emissions from this source were estimated to be 5.4 MMTCE for 1996, or 5 percent of U.S. N$_2$O emissions (see Table 3-26).

Adipic acid production reached its highest level in twelve years in 1996, growing about 2 percent from the previous year. Though production may continue to increase in the future, emissions should follow a significantly different path by the end of 1997, due to the widespread installation of pollution control measures mentioned above.

Table 3-26: N$_2$O Emissions from Adipic Acid Manufacture

Year	MMTCE	Gg
1990	4.7	56
1991	4.9	58
1992	4.6	54
1993	4.9	58
1994	5.2	62
1995	5.2	62
1996	5.4	63

Methodology

Nitrous oxide emissions were calculated by multiplying adipic acid production by the ratio of N_2O emitted per unit of adipic acid produced and adjusting for the actual percentage of N_2O released as a result of plant specific emission controls. Because emissions of N_2O in the United States are not regulated, emissions have not been well characterized. However, on the basis of experiments (Thiemens and Trogler 1991), the overall reaction stoichiometry for N_2O production in the preparation of adipic acid was estimated at approximately 0.3 kg of N_2O per kilogram of product.

Data Sources

Adipic acid production data for 1990 through 1995 (see Table 3-27) were obtained from *Chemical and Engineering News*, "Facts and Figures" and "Production of Top 50 Chemicals" (C&EN 1992, 1993, 1994, 1995, 1996). The 1996 data were projected from the 1995 manufactured total based upon suggestions of industry contacts. The emission factor was taken from Thiemens, M.H. and W.C. Trogler (1991).

Table 3-27: Adipic Acid Manufacture

Year	Thousand Metric Tons
1990	735
1991	771
1992	708
1993	765
1994	815
1995	816
1996	835

Uncertainty

Because N_2O emissions are controlled in some adipic acid production facilities, the amount of N_2O that is actually released will depend on the level of controls in place at a specific production plant. Thus, in order to calculate accurate emission estimates, it is necessary to have production data on a plant-specific basis. In most cases, however, these data are confidential. As a result, plant-specific production figures were estimated by allocating total adipic acid production using existing plant capacities. This creates a degree of uncertainty in the adipic acid production data used to derive the emission estimates as it is necessary to assume that all plants operate at equivalent utilization levels.

The emission factor was based on experiments (Thiemens and Trogler 1991) that attempt to replicate the industrial process and, thereby, measure the reaction stoichiometry for N_2O production in the preparation of adipic acid. However, the extent to which the lab results are representative of actual industrial emission rates is not known.

Nitric Acid Production

Nitric acid (HNO_3) is an inorganic compound used primarily to make synthetic commercial fertilizer. It is also a major component in the production of adipic acid— a feedstock for nylon—and explosives. Virtually all of the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia (EPA 1997). During this reaction, N_2O is formed as a by-product and is released from reactor vents into the atmosphere. While the waste gas stream may be cleaned of other pollutants such as nitrogen dioxide, there are currently no control measures aimed at eliminating N_2O.

Nitric acid production reached 8,252 thousand metric tons in 1996 (C&EN 1997). Nitrous oxide emissions from this source were estimated at 3.8 MMTCE, accounting for approximately 4 percent of U.S. N_2O emissions (see Table 3-28). Nitric acid production for 1996 increased 3 percent from the previous year, or 12 percent since 1990.

Table 3-28: N_2O Emissions from Nitric Acid Manufacture

Year	MMTCE	Gg
1990	3.4	40
1991	3.3	40
1992	3.4	40
1993	3.5	41
1994	3.7	44
1995	3.7	44
1996	3.8	45

Methodology

Nitrous oxide emissions were calculated by multiplying nitric acid production by the amount of N_2O emitted per unit of nitric acid produced. Off-gas measurements at one nitric acid production facility showed N_2O emission rates to be approximately 2 to 9 g N_2O per kg of nitric acid produced (Reimer et al. 1992). In calculating emissions, the midpoint of this range was used (5.5 kg N_2O/metric ton HNO_3).

Data Sources

Nitric acid production data for 1990 through 1996 (see Table 3-29) were obtained from *Chemical and Engineering News*, "Facts and Figures" and "Production of Top 50 Chemicals" (C&EN 1992, 1993, 1994, 1995, 1996). The emission factor range was taken from Reimer, R.A., Parrett, R.A., and Slaten, C.S. (1992).

Table 3-29: Nitric Acid Manufacture

Year	Thousand Metric Tons
1990	7,257
1991	7,189
1992	7,298
1993	7,488
1994	8,005
1995	8,023
1996	8,252

Uncertainty

These emission estimates are highly uncertain due to a lack of information on manufacturing processes and emission controls. Although no abatement techniques are specifically directed at removing N_2O at nitric acid plants, existing control measures for other pollutants may have some impact upon N_2O emissions. The emission factor range of 2 to 9 g N_2O per kg of nitric acid produced is significant, leading to further uncertainty when applying the midpoint value.

Substitution of Ozone Depleting Substances

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used primarily as alternatives to several classes of ozone-depleting substances (ODSs) that are being phased out under the terms of the *Montreal Protocol* and the Clean Air Act Amendments of 1990[12]. Ozone depleting substances—chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl chloroform, and hydrochloro-fluorocarbons (HCFCs)—are used in a variety of industrial applications including refrigeration and air conditioning equipment, solvent cleaning, foam production, sterilization, fire extinguishing, and aerosols. Although HFCs and PFCs, unlike ODSs, are not harmful to the stratospheric ozone layer, they are powerful greenhouse gases. Emission estimates for HFCs and PFCs used as substitutes for ODSs are provided in Table 3-30 and Table 3-31.

In 1990 and 1991, the only significant emissions of HFCs and PFCs as substitutes to ODS were relatively small amounts of HFC-152a—a component of the refrigerant blend R-500 used in chillers—and HFC-134a in refrigeration end-uses. Beginning in 1992, HFC-134a was used in growing amounts as a refrigerant in motor vehicle air conditioners and in refrigerant blends such as R-404[13]. In 1993, use of HFCs in foams and aerosols began, and in 1994 these compounds also found applications as solvents and sterilants. In 1995, ODS substitutes for halons entered widespread use in the United States as halon production was phased-out.

The use and subsequent emissions of HFCs and PFCs as ODS substitutes increased dramatically, from small amounts in 1990, to 11.9 MMTCE in 1996. This increase was the result of efforts to phase-out CFCs and other ODSs in the United States. This trend is expected to continue for many years, and will accelerate in the early part of the next century as HCFCs, which are interim substitutes in many applications, are themselves phased-out under the provisions of the Copenhagen Amendments to the *Montreal Protocol*.

---

[12] [42 U.S.C § 7671, CAA § 601]

[13] R-404 contains HFC-125, HFC-143a, and HFC-134a.

Table 3-30: Emissions of HFCs and PFCs from ODS Substitution (MMTCE)

Gas	1990	1991	1992	1993	1994	1995	1996
HFC-23	+	+	+	+	+	+	0.1
HFC-125	+	+	0.2	0.4	1.2	2.2	2.4
HFC-134a	0.2	0.2	0.2	1.0	1.9	3.4	4.8
HFC-143a	+	+	+	+	+	0.1	0.2
HFC-152a	0.1	+	+	+	+	+	+
HFC-227ea	+	+	+	+	0.7	1.5	1.6
HFC-236fa	+	+	+	+	+	+	0.1
HFC-4310mee	+	+	+	+	+	0.2	0.4
C_4F_{10}	+	+	+	+	+	+	0.1
C_6F_{14}	+	+	+	+	+	+	+
PFC/PFPEs*	+	+	+	+	0.1	2.0	2.0
Total	**0.3**	**0.2**	**0.4**	**1.4**	**4.0**	**9.5**	**11.9**

+ Does not exceed 0.05 MMTCE
* PFC/PFPEs are a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solventapplications. For estimating purposes, the GWP value used was based upon C_6F_{14}.
Note: Totals may not sum due to independent rounding.

Table 3-31: Emissions of HFCs and PFCs from ODS Substitution (Mg)

Gas	1990	1991	1992	1993	1994	1995	1996
HFC-23	+	+	+	+	+	9	26
HFC-125	+	+	236	481	1,628	2,823	3,172
HFC-134a	564	564	626	2,885	5,410	9,553	13,605
HFC-143a	+	+	+	12	43	94	226
HFC-152a	1,500	750	313	694	833	981	1,085
HFC-227ea	+	+	+	+	894	1,895	2,063
HFC-236fa	+	+	+	+	+	+	79
HFC-4310mee	+	+	+	+	+	611	1,030
C_4F_{10}	+	+	+	+	+	22	64
C_6F_{14}	+	+	+	+	+	2	6
PFC/PFPEs*	+	+	+	+	33	990	990

+ Does not exceed 0.5 Mg
* PFC/PFPEs are a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

Methodology and Data Sources

The EPA used a detailed vintaging model of ODS-containing equipment and products to estimate the use and emissions of various ODS substitutes, including HFCs and PFCs. The name of the model refers to the fact that the model tracks the use and emissions of various compounds for the annual "vintages" of new equipment that enter service in each end-use. This vintaging model predicts ODS and ODS substitute use in the United States based on modeled estimates of the quantity of equipment or products sold each year containing these chemicals and the amount of the chemical required to manufacture and/or maintain equipment and products over time. Emissions for each end-use were estimated by applying annual leak rates and release profiles. By aggregating the data for more than 40 different end-uses, the model produces estimates of annual use and emissions of each compound.

The major end-use categories defined in the vintaging model to characterize ODS use in the United States were: refrigeration and air conditioning, aerosols, solvent cleaning, fire extinguishing equipment, sterilization, and foams.

The vintaging model estimates HFC and PFC use and emissions resulting from their use as replacements for ODS by undertaking the following steps:

Step 1: Estimate ODS Use in the United States Prior to Phase-out Regulations

The model begins by estimating chlorofluorocarbon (CFC), halon, methyl chloroform, and carbon tetrachloride use prior to the restrictions on the production of these compounds in the United States. For modeling purposes, total ODS use was divided into more than 40 separate end-uses. The methodology used to estimate baseline ODS use varied depending on the end-use under consideration. The next section describes the methodology used for estimating baseline ODS use in the refrigeration, air conditioning, and fire extinguishing (halon) sectors. The subsequent section details the methodology used for all other end-uses.

Step 1.1: Estimate Baseline ODS Use for Refrigeration, Air Conditioning, and Fire Extinguishing

For each equipment type, the model estimates the total stock of ODS-containing equipment during the period 1985 to 1996. The key data required to develop stock estimates for each end-use were as follows:

- Total stock of ODS-containing equipment in use in the United States in 1985
- The annual rate of growth in equipment consumption in each end-use
- The retirement function for equipment in each end-use

Historical production and consumption data were collected for each equipment type to develop estimates of total equipment stock in 1985. For some end-uses, the only data available were estimates of ODS usage. In these cases, the total 1985 stock was estimated by dividing total ODS use by the average charge of ODS in a typical piece of equipment.

Stocks of ODS-containing equipment change over time. In the vintaging model, the growth in equipment stocks in each end-use was simulated after 1985 using growth rates that define the total number of pieces of new equipment added to the stock each year. The model also uses a retirement function to calculate the length of time each piece of equipment is expected to remain in service. These retirement functions are a critical part of the vintaging model because they determine the speed at which the stock of equipment turns over and is replaced by new equipment. In this analysis, point estimates of the average lifetime of equipment in each end-use were used to develop retirement functions. These retirement functions assume 100 percent survival of equipment up to this average age and zero percent survival thereafter.

Given these data, the total equipment stock in service in a given year t was estimated as the equipment stock in the year (t-1), plus new equipment added to the stock in year t, minus retirements in year t.

Annual ODS use was then estimated for each equipment type during the period 1985 through 1996. Because control technologies can reduce particular kinds of ODS use, use estimates were broken down by type of use (e.g., use in new equipment at manufacture and use required to maintain existing equipment). Baseline estimates of ODS use were based on the following data collected for each equipment type:

- ODS charge size (Refers to the number of kilograms of ODS installed in new equipment during manufacture)
- ODS required to maintain existing equipment (In many end-uses, ODS must be regularly added to equipment to replace chemical emitted from the equipment. Such emissions result from normal leakage and from loss during servicing of the equipment.)

With these data, ODS usage for each refrigeration, air conditioning, and fire extinguishing end-use was calculated using the following equation:

(Total stock of existing equipment in use) X (ODS required to maintain each unit of existing equipment) + (New equipment additions) X (ODS charge size)

Step 1.2: Estimate Baseline ODS Use in Foams, Solvents, Sterilization, and Aerosol End-Uses

For end-uses other than refrigeration, air conditioning, and fire extinguishing, a simpler approach was used because these end-uses do not require partial re-filling of existing equipment each year. Instead, such equipment either does not require any ODS after initial production (e.g., foams and aerosols), or requires complete

re-filling or re-manufacturing of the equipment each year (e.g., solvents and sterilants). ODS use does not need to be differentiated between new and existing equipment for these end-uses. Thus, it is not necessary to track the stocks of new and existing equipment separately over time.

The approach used for these end-uses was to estimate total ODS use in 1985 based on available industry data. Future ODS use was estimated using growth rates that predict ODS consumption growth in these end-uses over time, based upon input from industry.

Step 2: Specification and Implementation of Control Technologies

Having established a baseline for ODS equipment in 1985, the vintaging model next defines controls that may be undertaken for purposes of reducing ODS use and emissions within each end-use. The following controls are implemented in the model:

- Replacement of ODS used in the manufacturing of new equipment or in the operation of existing equipment (i.e., retrofits) with alternative chemicals, such as HFCs and PFCs

- Replacement of ODS-based processes or products with alternative processes or products (e.g., the use of aqueous cleaning to replace solvent cleaning with CFC-113)

- Modification of the operation and servicing of equipment to reduce use and emission rates through the application of engineering and recycling controls

Assumptions addressing these types of controls in each end-use were used to develop "substitution scenarios" that simulate the phase-out of ODSs in the United States by end-use. These scenarios represent EPA's best estimates of the use of control technologies towards the phase-out ODS in the United States, and are periodically reviewed by industry experts.

In addition to the chemical substitution scenarios, the model also assumes that a portion of ODS substitutes are recycled during servicing and retirement of the equipment. Recycling is assumed to occur in the refrigeration and air conditioning, fire extinguishing, and solvent end-uses.

The substitution scenarios defined for each equipment type were applied to the relevant equipment stocks. The equipment life-cycle was then simulated after the imposition of controls. Substitute chemical use and emissions—including HFCs and PFCs—were calculated for each scenario using the methods described below.

Step 3: Estimate ODS Substitute Use and Emissions (HFCs and PFCs)

ODS substitute use (i.e., HFC and PFC use) was calculated using the same routine described above for refrigeration, air conditioning, and fire extinguishing equipment. In terms of chemical usage, a key question was whether implementation of a given ODS substitute in an end-use changed the quantity of chemical required to manufacture new equipment or service existing equipment. In this analysis, it was assumed that the use of ODS alternatives in new equipment—including HFCs and PFCs—did not change the total charge of initial chemical used in the equipment in each end-use. For certain refrigeration and air conditioning end-uses, however, it was assumed that new equipment manufactured with HFCs and PFCs would have lower leak rates than older equipment. Existing ODS-containing equipment that was retrofitted with HFCs or PFCs was assumed to have a higher leak rate than new HFC/PFC equipment.

The use of HFCs and PFCs in all other sectors was calculated by simply replacing ODS use with the chemical alternatives defined in the substitution scenarios. The use of HFCs and PFCs was not assumed to change the quantity of chemical used in new or existing equipment for these sectors.

The vintaging model estimates HFC and PFC emissions over the lifetime of equipment in each end-use. Emissions may occur at the following points in the lifetime of the equipment:

- Emissions upon manufacture of equipment
- Annual emissions from equipment (due to normal leakage, and if applicable, servicing of equipment)
- Emissions upon retirement of equipment

The emissions that occur upon manufacture of refrigeration and air conditioning equipment were assumed to be less than 0.1 percent. Annual emissions of HFCs and

PFCs from equipment—due to normal leakage and servicing—were assumed to be constant each year over the life of the equipment. The quantity of emissions at disposal is a function of the prevalence of recycling at disposal.

Emissions for open cell foam were assumed to be 100 percent in the year of manufacture. Closed cell foams were assumed to emit a portion of total HFC/PFC use upon manufacture, a portion at a constant rate over the lifetime of the foam, and the rest at disposal. There were no foam recycling technologies in use in the United States; therefore, HFCs and PFCs remaining in closed cell foam were assumed to be emitted by the end of the product lifetime.

Emissions were assumed to occur at manufacture, during normal operation, and upon retirement of fire extinguishing systems. Emissions at manufacture were assumed to be negligible and emissions upon disposal were assumed to be minimal because of the use of recovery technologies.

For solvent applications, 15 percent of the chemical used in equipment was assumed to be emitted in that year. The remainder of the used solvent was assumed to be disposed rather than emitted or recycled.

For sterilization applications, all chemicals that were used in the equipment were assumed to be emitted in that year.

All HFCs and PFCs used in aerosols were assumed to be emitted in the same year. No technologies were known to exist that recycle or recover aerosols.

Uncertainty

Given that emissions of ODS substitutes occur from thousands of different kinds of equipment and from millions of point and mobile sources throughout the United States, emission estimates must be made using analytical tools such as the EPA vintaging model or the methods outlined in IPCC/UNEP/OECD/IEA (1997). Though EPA's model is more comprehensive than the IPCC methodology, significant uncertainties still exist with regard to the levels of equipment sales, equipment characteristics, and end-use emissions profiles that were used to estimate annual emissions for the various compounds.

Aluminum Production

Aluminum is a light-weight, malleable, and corrosion resistant metal that is used in many manufactured products including aircraft, automobiles, bicycles, and kitchen utensils. The United States was the largest producer with 17 percent of the world total in 1996 (USGS 1997). The United States was also a major importer. The production of aluminum—in addition to consuming large quantities of electricity—results in emissions of several greenhouse gases including carbon dioxide (CO_2) and two perfluorocarbons (PFCs): perfluoromethane (CF_4) and perfluoroethane (C_2F_6).

Occasionally, sulfur hexafluoride (SF_6) is also used by the aluminum industry as a degassing agent in specialized applications. In these cases it is mixed with argon and nitrogen and blown through molten aluminum as it cools; however, this practice is not know to be used by firms in the United States. Where it does occur in other countries, the concentration of SF_6 in the mixture is small and it is believed that nearly all the SF_6 is destroyed in the process.

Carbon dioxide is emitted during the aluminum smelting process when alumina (aluminum oxide, Al_2O_3) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a molten bath of natural or synthetic cryolite (Na_3AlF_6). The reduction cells contain a carbon lining that serves as the cathode. Carbon is also contained in the anode, which can be a carbon mass of paste, coke briquettes, or prebaked carbon blocks from petroleum coke. During reduction, some of this carbon is oxidized and released to the atmosphere as CO_2.

Process emissions of CO_2 from aluminum production were estimated at 1.4 MMTCE (5.3 Tg) in 1996 (see Table 3-32). The CO_2 emissions from this source, however, are accounted for under the non-fuel use portion of CO_2 from Fossil Fuel Combustion of petroleum coke and tar pitch in the Energy sector. Thus, to avoid double counting, CO_2 emissions from aluminum production are not included in totals for the Industrial Processes sector. They are described here for informational purposes only.

Table 3-32: CO_2 Emissions from Aluminum Production

Year	MMTCE	Tg
1990	1.6	6.0
1991	1.7	6.1
1992	1.6	5.9
1993	1.5	5.4
1994	1.3	4.8
1995	1.4	5.0
1996	1.4	5.3

Table 3-34: PFC Emissions from Aluminum Production (Mg)

Year	CF_4	C_2F_6
1990	2,430	240
1991	2,330	230
1992	2,020	200
1993	1,750	170
1994	1,400	140
1995	1,330	130
1996	1,430	140

In addition to CO_2 emissions, the aluminum production industry was also the largest source of PFC emissions in the United States. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, termed "anode effects". These anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of CF_4 and C_2F_6. In general, the magnitude of emissions for a given level of production depends on the frequency and duration of these anode effects. The more frequent and long-lasting the anode effects, the greater the emissions.

Primary aluminum production related emissions of PFCs are estimated to have declined from 4.3 MMTCE of CF_4 (2,430 Mg) and 0.6 MMTCE of C_2F_6 (240 Mg) in 1990 to 2.5 MMTCE of CF_4 (1,430 Mg) and 0.4 MMTCE of C_2F_6 (140 Mg) in 1996, as shown in Table 3-33 and Table 3-34. The overall decline in PFC emissions is estimated to have been 40 percent. This decline was both due to reductions in domestic aluminum production and actions taken by aluminum smelting companies to reduce the frequency and duration of anode effects under EPA's Voluntary Aluminum Industrial Partnership

Table 3-33: PFC Emissions from Aluminum Production (MMTCE)

Year	CF_4	C_2F_6	Total
1990	4.3	0.6	4.9
1991	4.1	0.6	4.7
1992	3.6	0.5	4.1
1993	3.1	0.4	3.5
1994	2.5	0.4	2.8
1995	2.4	0.3	2.7
1996	2.5	0.4	2.9

Note: Totals may not sum due to independent rounding.

(VAIP).

U.S. primary aluminum production for 1996, totaling 3,577 thousand metric tons, increased by 6 percent from 1995 to 1996. Production fell to a seven-year low in 1994, continuing a decline which started in 1991. These declines were due in part to a continued increase in imports, primarily from the former Soviet Union. For example, in 1994 these countries exported 60 percent more ingots (metal cast for easy transformation) to the United States than in 1993. However, the U.S. Geological Survey (USGS) reported that this supply surplus would be temporary and that a more normal global supply and demand equilibrium should return beginning in 1995. Data for 1995 and 1996 appear to support this assessment. U.S. imports for consumption of aluminum materials decreased in 1996 compared with those of the previous year. Although imports from Russia continued to decline from their peak level in 1994, Russia remained the second largest source of imports (USGS 1997).

The transportation industry remained the largest domestic consumer of aluminum, accounting for about 28 percent (USGS 1997). The "big three" automakers have announced new automotive designs that will expand the use of aluminum materials in the near future. USGS believes that demand for and production of aluminum should continue to increase.

Methodology

Carbon dioxide is released to the atmosphere during alumina reduction to aluminum metal following the reaction below:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

The quantity of CO_2 released was estimated from

the production volume of primary aluminum metal and the carbon consumed by the process. During alumina reduction, approximately 1.5 to 2.2 metric tons of CO_2 are emitted for each metric ton of aluminum produced (Abrahamson 1992). In previous inventories, the mid-point (1.85) of this range was used for the emission factor. However, for this year's report—and adjusting earlier years—the emission factor was revised to 1.5 metric tons CO_2 per metric ton of aluminum smelted based on a mass balance for a "typical" aluminum smelter (Drexel University Project Team 1996). This value is at the low end of the Abrahamson (1992) range.

The CO_2 emissions from this source are already accounted for under CO_2 Emissions from Fossil Fuel Combustion in the Energy sector.[14] Thus, to avoid double counting, CO_2 emissions from aluminum production are not included in totals for the Industrial Processes sector.

PFC emissions from aluminum production were estimated using a per unit production emission factor for the base year 1990. The emission factor used is a function of several operating variables including average anode effect frequency and duration. Total annual emissions for 1990 were then calculated based on reported annual production levels. The five components of the per unit production emission factor are:

- Amount of CF_4 and C_2F_6 emitted during every minute of an anode effect, per ampere of current
- Average duration of anode effects
- Average frequency of anode effects
- Current efficiency for aluminum smelting
- Current required to produce a metric ton of aluminum, assuming 100 percent efficiency

Using available data for the United States, this methodology yields a range in the emission factor of 0.01 to 1.2 kg CF_4 per metric ton of aluminum produced in 1990 (Jacobs 1994). The emission factor for C_2F_6 was estimated to be approximately an order of magnitude lower. Emissions for 1991 through 1996 were estimated with emission factors that incorporated data on reductions in anode effects re-

ported to the VAIP by aluminum companies.

Data Sources

Production data for 1990 through 1996 (see Table 3-35) were obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1997, 1995). The USGS requested data from the 13 domestic producers, all of whom responded. The CO_2 emission factor range was taken from Abrahamson (1992). The mass balance for a "typical" aluminum smelter was taken from Drexel University Project Team (1996).

PFC emission estimates were provided by the EPA's Atmospheric Pollution Prevention Division in coopera-

Table 3-35: Production of Primary Aluminum

Year	Thousand Metric Tons
1990	4,048
1991	4,121
1992	4,042
1993	3,695
1994	3,299
1995	3,375
1996	3,577

tion with participants in the Voluntary Aluminum Industrial Partnership.

Uncertainty

Uncertainty exists as to the most accurate CO_2 emission factor for aluminum production. Emissions vary depending on the specific technology used by each plant. However, evidence suggests that there is little variation in CO_2 emissions from plants utilizing similar technologies (IPCC/UNEP/OECD/IEA 1997). A less uncertain method would be to calculate emissions based upon the amount of carbon—in the form of petroleum coke or tar pitch—consumed by the process; however, this type of information was not available.

---

[14] Although the carbon contained in the anode is considered a non-fuel use of petroleum coke or tar pitch and should be included in the Industrial Processes sector, information to distinguish individual non-fuel uses of fossil fuels is unfortunately not available in DOE/EIA fuel statistics.

For PFC emission estimates, the value for emissions per anode effect minute per ampere was based on a limited number of measurements that may not be representative of the industry as a whole (EPA 1993). For example, the emission factor may vary by smelter technology type, among other factors. The average frequency of anode effects and the current efficiency are well documented; however, insufficient measurement data existed to quantify a relationship between PFC emissions and anode effect minutes. Future inventories will incorporate additional data reported to VAIP by aluminum companies and ongoing research into PFC emissions from aluminum production.

HCFC-22 Production

Trifluoromethane (HFC-23 or CHF_3) is generated as a by-product during the manufacturing of chlorodifluoromethane (HCFC-22), which is currently used both as a substitute for ozone depleting substances—mainly in refrigeration and air conditioning systems—and as a chemical feedstock for manufacturing synthetic polymers. Although HCFC-22 production is scheduled to be phased out by 2020 under the U.S. Clean Air Act[15] because of its stratospheric ozone depleting properties, feedstock production is permitted to continue indefinitely.

Emissions of HFC-23 in 1996 were estimated to be 8.5 MMTCE (2,660 Mg). This represents over a 10 percent decline from emissions in 1990 (see Table 3-36).

In the future, production of HCFC-22 is expected to initially increase in the United States and then decline as non-feedstock HCFCs production is phased-out; feedstock production is anticipated to continue growing steadily, mainly for manufacturing Teflon[Ò] and other chemical products. All U.S. producers of HCFC-22 are participating in a voluntary program with the EPA to reduce HFC-23 emissions.

Methodology

EPA studied the conditions of HFC-23 generation, methods for measuring emissions, and technologies for emissions control. This effort was undertaken in cooperation with the manufacturers of HCFC-22.

Previous emission estimates assumed that HFC-23 emissions were between 2 and 4 percent of HCFC-22 production on a mass ratio basis. The methodology employed for this year's inventory was based upon measurements of critical feed components at individual HCFC-22 production plants. Individual producers also measured HFC-23 concentrations in the process stream by gas chromatography. Using measurements of feed components and HFC-23 concentrations in process streams, the amount of HFC-23 generated was estimated. HFC-23 concentrations were determined at the point the gas leaves the chemical reactor; therefore, estimates also include fugitive emissions.

Data Sources

Emission estimates were provided by the EPA's Atmospheric Pollution Prevention Division in cooperation with the U.S. manufacturers of HCFC-22.

Uncertainty

A high level of confidence has been attributed to the HFC-23 concentration data employed because measurements were conducted frequently and accounted for day-to-day and process variability. It is estimated that the emissions reported are within 20 percent of the true value. This methodology allowed for determination of reductions in HFC-23 emissions during a period of increasing HCFC-22 production. (Use of emission factors would not have allowed for such an assessment.) By

Table 36: HFC-23 Emissions from HCFC-22 Production

Year	MMTCE	Mg
1990	9.5	2,980
1991	8.4	2,630
1992	9.5	2,980
1993	8.7	2,730
1994	8.6	2,700
1995	7.4	2,320
1996	8.5	2,660

---

15 As construed, interpreted and applied in the terms and conditions of the *Montreal Protocol on Substances that Deplete the Ozone Layer*. [42 U.S.C. §7671m(b), CAA §614]

1996, the rate of HFC-23 generated as a percent of HCFC-22 produced dropped, on average, below 2 percent in the United States.

Semiconductor Manufacture

The semiconductor industry uses multiple long-lived fluorinated gases in plasma etching and chemical vapor deposition (CVD) processes. The gases most commonly employed are trifluoromethane (HFC-23), perfluoromethane (CF_4), perfluoroethane (C_2F_6), and sulfur hexafluoride (SF_6), although other compounds such as nitrogen trifluoride (NF_3) and perfluoropropane (C_3F_8) are also used. The exact combination of compounds is specific to the process employed.

For 1996, it was estimated that total weighted emissions of all greenhouse gases by the U.S. semiconductor industry was 1.3 MMTCE. These gases were not widely used in 1990, hence, emissions in 1990 were estimated to

Table 3-37: PFC Emissions from Semiconductor Manufacture

Year	MMTCE*
1990	0.2
1991	0.4
1992	0.6
1993	0.8
1994	1.0
1995	1.2
1996	1.4

* Combined radiative forcing effect of all gases

be only 0.2 MMTCE. Combined emissions of all gases are presented in Table 3-37 below. It is expected that the rapid growth of this industry and the increasing complexity of microchips will increase emissions in the future.

Methodology

An estimate of emissions was developed based on the approximate sales of the four main gases (HFC-23, CF_4, C_2F_6, and SF_6) to semiconductor firms. Estimates were confirmed with data reported to the EPA by a subset of firms in the industry who have engaged in voluntary monitoring efforts. Further study of gas emission rates is also underway.

Data Sources

Emission estimates were provided by the EPA's Atmospheric Pollution Prevention Division in cooperation with the U.S. semiconductor industry.

Uncertainty

Emission estimates for this source are believed to be highly uncertain due to the lack of detailed gas consumption data and the complex chemical reactions involved in the processes used. For example, in the etching process the gas molecules are disrupted by a plasma into varied recombinant formulations specific to each tool and operation.

Because of the uncertainties surrounding its contribution to the greenhouse gas effect, NF_3 is not included in this inventory of greenhouse gas emissions. It has been estimated that the atmospheric lifetime of NF_3, before it undergoes photodissociation in the stratosphere, is about 700 years, resulting in a 100 year global warming potential (GWP) value of approximately 8,000 (Molina, Wooldridge, and Molina 1995). As the understanding of the emission characteristics of this gas improves, NF_3 will be included in future inventories.

Electrical Transmission and Distribution

The largest use for sulfur hexafluoride (SF_6), both domestically and internationally, is as an electrical insulator in equipment that transmits and distributes electricity. It has been estimated that eighty percent of the worldwide use of SF_6 is in electrical transmission and distribution systems (Ko et al. 1993). The gas has been employed by the electric power industry in the United States since the 1950s because of its dielectric strength and arc-quenching characteristics. It is used in gas-insulated substations, circuit breakers, and other switchgear. Sulfur hexafluoride has replaced flammable insulating oils in many applications and allows for more compact substations in dense urban areas.

Fugitive emissions of SF_6 can escape from gas-insulated substations and gas-insulated circuit breakers through seals, especially from older equipment. It can also be released when equipment is opened for servic-

Table 3-38: SF$_6$ Emissions from Electrical Transmission and Distribution

Year	MMTCE	Mg
1990	5.6	859
1991	5.9	902
1992	6.2	945
1993	6.4	988
1994	6.7	1,031
1995	7.0	1,074
1996	7.0	1,074

ing, which typically occurs every few years. In the past, some utilities vented SF$_6$ to the atmosphere during servicing; however, it is believed that increased awareness and the relatively high cost of the gas have reduced this practice.

Emissions of SF$_6$ from electrical transmission and distribution systems was estimated to be 7.0 MMTCE (1,020 Mg) in 1996. This quantity amounts to a 25 percent increase over the estimate for 1990 (see Table 3-38).

Methodology

Manufacturers of circuit breakers and gas-insulated substations have claimed that new equipment leaks at rates of less than 1 percent annually. To explore emission rates from electrical equipment, the EPA examined atmospheric concentrations of SF$_6$. Assumptions were made to estimate historical worldwide SF$_6$ production. Based on measured concentrations, an atmospheric mass balance was then calculated. This mass balance provided an indication that most of the SF$_6$ produced worldwide since the early 1950s must have been emitted. Thus, it was concluded that emission rates from equipment must be higher than had been claimed. It was assumed that roughly three-quarters of SF$_6$ production was used in electrical equipment and that equipment leaked at a rate much higher than proposed by industry.

Data Sources

Emission estimates were provided by the EPA's Atmospheric Pollution Prevention Division in cooperation with the U.S. electric utilities.

Uncertainty

There is little verifiable data existing for estimat-

ing SF$_6$ emissions from electrical transmission and distribution systems. Neither gas consumption nor leakage monitoring data were available. An accurate inventory of the stock of SF$_6$ in existing equipment, in addition to improved assumptions of the leak rates from both new and old equipment, will be required to develop improved emission estimates.

Magnesium Production and Processing

The magnesium metal production and casting industries use sulfur hexafluoride (SF$_6$) as a covergas to prevent the violent oxidation of molten magnesium in the presence of air. Small concentrations of SF$_6$ in combinations with carbon dioxide and air are blown over the molten magnesium metal to induce the formation of a protective crust. The industry adopted the use of SF$_6$ to replace sulfur dioxide (SO$_2$). The SF$_6$ technique is used by producers of primary magnesium metal and most magnesium part casters. The recycling industry, for the most part, continues to employ sulfur dioxide as a covergas.

For 1996, a total of 3.0 MMTCE (460 Mg) of SF$_6$ was estimated to have been emitted by the magnesium industry, 76 percent more than was estimated for 1990 (see Table 3-39). There are no significant plans for expansion of primary production in the United States, but demand for magnesium metal for die casting has the potential to expand if auto manufacturers begin designing more magnesium parts into future vehicle models.

Methodology

Emissions were estimated based upon usage infor-

Table 3-39: SF$_6$ Emissions from Magnesium Production and Processing

Year	MMTCE	Mg
1990	1.7	260
1991	2.0	300
1992	2.2	340
1993	2.5	380
1994	2.7	420
1995	3.0	460
1996	3.0	460

mation supplied to the EPA by primary magnesium producers. Consumption was assumed to equal emissions in the same year. Although not directly employed, the Norwegian Institute for Air Research (NIAR 1993) has reported a range of emission factors for primary magnesium production as being from 1 to 5 kg of SF_6 per metric ton of magnesium. A survey of magnesium die casters has also reported an average emission factor of 4.1 kg of SF_6 per metric ton of magnesium parts die cast (Gjestland and Magers 1996).

Data Sources

Emission estimates were provided by the EPA's Atmospheric Pollution Prevention Division in cooperation with the U.S. primary magnesium metal producers and casting firms.

Uncertainty

There are a number of uncertainties in these estimates, including the assumption that SF_6 does not react nor decompose during use. In reality, it is possible that the high temperatures associated with molten magnesium would cause some gas degradation. Like other sources of SF_6 emissions, verifiable SF_6 consumption data were not available.

Industrial Sources of Criteria Pollutants

In addition to the main greenhouse gases addressed above, many industrial processes generate emissions of criteria air pollutants. Total emissions of nitrogen ox-

ides (NO_x), carbon monoxide (CO), and nonmethane volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 1996 are reported by detailed source category in Table 3-40.

Methodology and Data Sources

The emission estimates for this source were taken directly from the EPA's *National Air Pollutant Emissions Trends, 1900-1996* (EPA 1997a). Emissions were calculated either for individual sources or for many sources combined, using basic activity data (e.g., the amount of raw material processed) as an indicator of emissions. National activity data were collected for individual source categories from various agencies. Depending on the source category, these basic activity data may include data on production, fuel deliveries, raw material processed, etc.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the EPA's *Compilation of Air Pollutant Emission Factors, AP-42* (EPA 1997b). The EPA currently derives the overall emission control efficiency of a source category from a variety of information sources, including published reports, the 1985 National Acid Precipitation and Assessment Program emissions inventory, and other EPA databases.

Uncertainty

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and accurate estimates of activity data.

Table 3-40: Emissions of NO$_x$, CO, and NMVOC from Industrial Processes (Gg)

Gas/Source	1990	1991	1992	1993	1994	1995	1996
NO$_x$	**923**	**802**	**784**	**760**	**933**	**815**	**821**
Chemical & Allied Product							
Manufacturing	152	149	148	141	145	144	144
Metals Processing	88	69	74	75	82	89	89
Storage and Transport	3	5	4	4	5	5	5
Other Industrial Processes	343	319	328	336	353	362	366
Miscellaneous*	337	259	230	204	347	215	217
CO	**9,580**	**7,166**	**5,480**	**5,500**	**7,787**	**5,370**	**5,379**
Chemical & Allied Product							
Manufacturing	1,074	1,022	1,009	992	1,063	1,109	1,109
Metals Processing	2,395	2,333	2,264	2,301	2,245	2,159	2,157
Storage and Transport	69	25	15	46	22	22	22
Other Industrial Processes	487	497	494	538	544	566	576
Miscellaneous*	5,556	3,288	1,697	1,623	3,912	1,514	1,514
NMVOCs	**3,193**	**2,997**	**2,825**	**2,907**	**3,057**	**2,873**	**2,299**
Chemical & Allied Product							
Manufacturing	575	644	649	636	627	599	396
Metals Processing	111	112	113	112	114	113	64
Storage and Transport	1,356	1,390	1,436	1,451	1,478	1,499	1,190
Other Industrial Processes	364	355	376	401	397	409	398
Miscellaneous*	787	496	252	306	441	253	251

* Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, TSDFs (Transport, Storage, and Disposal Facilities under the Resource Conservation and Recovery Act), cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Agricultural Burning source.
Note: Totals may not sum due to independent rounding.